CHAPTER-1

INTRODUCTION
1. INTRODUCTION

Nature manifests itself in a wide spectrum of rainbow colors. Man-fascinated by her glory, strove towards harmonizing with her completely. He internalized colors by responding to its vibrations emotionally and externally, he drew from her vast store house, to initially paint himself and then to dye the apparel he wore.

Thus started the alchemy of color and India was a fore runner in the art of natural dyeing the era of the great epics. Through this ancient art withstood the ravages of time, with the discovery of the first synthetic dyes in 1856, a rapid decline in natural dye set in.

Synthetic dyes received faster acceptability due to its ease in dyeing, reproducibility and cost factors. Thus it took barely century to erode almost all traces of natural dyes from the sub continent. But in the late 1994, Germany struck a severe blow to dyestuff industry and subsequently European countries, by executing ban on import of textile and garments colored with series of azo dyes made from aromatic amines which are carcinogenic, allergenic and poisonous.

Use of synthetic dye involves release of enormous amount of hazardous chemicals in the environment during their production and subsequent use. With the environmentally benign products becoming a top priority in recent years, dye industry has turned its attention to newer products, which cater to fashion trends as well as to environmental specifications. Recent ban on production and use of unsubstituted benzidine, an important intermediate for direct dyes possessing carcinogenic properties, has led all major intermediates
manufacturers to search for benign alternatives. The EEC has promulgated the "EC control of substance hazardous to health act 1989" and published a red list enumerating a number of chemicals, the presence of which in any kind of fabric has been banned. Similarly an ordinance of German Government stipulated that no garment or any other article that comes into contact with the skin shall contain any of the 22 amines named there under. Thus making Natural Dyes as the safest alternatives and fortunately India has an advantageous position since the country holds a rich reservoir of natural resources with potential dyestuff products. Because of tropical climate we can grow a large number of dye yielding plants, however the problems encountered in the use of natural dyes are as follows:

- Non-availability because of difficulty of collection and standardization of dyes.
- Bulk isolation of dyestuff
- Shade variation
- Standardization of dyes on fabric by using non-toxic mordants.

However it is our good luck that even now in some remote areas of our country, natural dyeing is still alive and flourishing. Knowledge and skill that had required thousands of years of experimentation and refinement were not forgotten. Thus unlocking of natural secret colors has not completely become a lost art. With the advent of synthetic dyes and their immediate acceptability throughout the world, the use of natural dyes is still continued in selected pockets of India as a small-
scale industry. World wide there is a drive for Natural Dyes but only India and few other Asian countries have the expertise and raw material.

Natural dyes are derived from plants, insects and minerals. The use of such coloring matter is rooted in antiquity. Shades produced are rich and soothing, some of the important natural dyes are extracted from materials, which are hitherto neglected as waste materials. Natural dyes are biodegradable, non-toxic, and environment friendly, aesthetically appealing resulting in employment generation and utilization of wasteland.

Many of the natural dyes give different shades in conjugation with inorganic salts. For example, the coloring matter derived from the roots of madder plant is Alizarin. This substance is a polygenic dye, which produces different colors with various mordants, it gives red shades varying from purple to black. Thus we see the role played by mordant is important. We also know that the demand of dye industry is very high. Cultivation of large area of land with dye yielding plants will also not suffice the need. Thus the synthesis of Natural Dyes in the laboratory using eco-friendly process has become a matter of prime importance.
Sources of Natural Dyes:
The great availability of natural dyes historically has depended on four sources:

1) Specialized plants and animal sources: Many plants and some animals have been identified as potentially rich in natural dye contents, some of them have been used for natural dyeing for quite some time.

2) By products (especially lac dye): Lac has many and varied industrial uses. The lac industry gives lac as a by-product. This was considered as a waste till dye was extracted from the effluent. Similarly Cassia tora, which is used in gum manufacturing process, also yields a brown colored dye as by-product.

3) Chemical synthesis: After the structure elucidation of some of the important natural colorants, chemists worldwide have been synthesizing these naturally occurring dyes in laboratory. Chemical synthesis has provided the carotenoids, canthaxthin, carotene, 8-apocarotenal and ethyl 8-apocarotenate and a range of indigoids. These chemicals synthesis have been proved to be highly environmentally harmful unless the process routes are carefully developed. We have synthesized two series of dyes using microwave technology in our laboratory. These syntheses are an improvement over the existing ones in terms of yields and reaction time. We have even tried to minimize the use of hazardous chemicals and make use of non-conventional source of energy such as microwave radiation.
4) Tissue or cell culture by DNA transfer biotechnology: Anthraquinone compounds, important in dyestuff industry have been identified as secondary metabolites are produced by some fungi such as *Drechslera, Trichoderma*. Exploiting the fungal synthesis of anthraquinone has several advantages over chemical methods. The medium in which the fungal culture grows contains no expensive chemicals. The fermentation is carried out at low temperature 30°C and at neutral pH. Anthraquinone compounds with chloro or amino substitution would be useful for dye production, but are not common among fungal anthraquinone. It is possible that these compounds may be engineered by genetic modification.

The two most ecofriendly approach to natural dye manufacturing are:

- By enriching the natural sources by efficient cultivation techniques and extraction techniques.

- Bio-technological methods to obtain safer natural structural entities in an inherent natural way.

Since microwave irradiation, an ecofriendly process, has recently become extremely popular to accelerate organic reactions. It provides high heat efficiency, remarkable rate enhancement, dramatic reduction in reaction times, it was considered using microwave irradiation in improving the synthesis of safe dyes. This latest technology is developed mainly for the drive towards synthesis of safe dyes.
Dyes are colored, ionizing, aromatic compounds and as such are based fundamentally on the structure of benzene. For a substance to act as a dye, certain conditions must be fulfilled that is

- It must have a suitable color.
- It must be able to fix itself or be capable of being fixed to the fabric.
- It must not be fugitive after fixing on the fabric to be dyed.
- It should have good washing, rubbing, light and perspiration fastness properties.

However the chemical synthesis has proved to be highly environmentally harmful unless the process routes are carefully developed and checked. The innumerable dyestuffs compounds that have been developed fall in either of the cases:

- Themselves hazardous (carcinogenic)
- Made by polluting process
- Obtained from carcinogenic intermediates
- Susceptible to degradation to harmful degraded products.

**Application of natural colorants:**

Solubility of natural colorants: Majority of the natural dyes have the hydroxyl group (OH) in their nucleus and are sparingly soluble in water. Increase in solubility may be obtained by adding an alkali such as sodium carbonate to the aqueous solution, some of the natural colorants do not have a solubility group, in this case a temporary
solubilising group is generated at the time of application. For example, in the case of indigo like a regular vat dye reduction and oxidation are carried out. The original dye structure reverts on the fabric.

As natural dyes are safe for environment and not many of these dyes have been explored, to combat this problem and to have a pollution free environment the present work is undertaken with the following objectives:

- To screen newer plant sources and to identify these sources for different colors.
- Chemical characterization of coloring matter of these new plant sources i.e. Sappan wood, Canna, Eucalyptus, Lac etc. and also the prevailing natural dye sources with extensive use of mordant.
- Solvent extraction of pigments using soxlet, sonicator and supercritical fluid extraction.
- Adsorption on solid support for the recycling of resources, a better dye yielding process with longer shelf life.
- Determining the use of proper mordants such as: 1) Metallic salts 2) Tannic acid
- Utilization of ultrasound energy for dyeing of cotton fabric.
- Development of synthetic safe dyes using microwave irradiation.